

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification³ : C08F 8/22, 255/02, 257/02</p>	<p>A1</p>	<p>(11) International Publication Number: WO 83/ 02617 (43) International Publication Date: 4 August 1983 (04.08.83)</p>
<p>(21) International Application Number: PCT/US83/00079 (22) International Filing Date: 17 January 1983 (17.01.83) (31) Priority Application Number: 344,143 (32) Priority Date: 29 January 1982 (29.01.82) (33) Priority Country: US (71) Applicant: MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US). (72) Inventor: WNEK, Gary, E. ; 2 Village Way, Natick, MA 01760 (US). (74) Agent: ENGELLENNER, Thomas, J.; MIT Patent Office, Room E19-722, Massachusetts Institute of Technology, Cambridge, MA 02139 (US).</p>		<p>(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i></p>
<p>(54) Title: ELECTRICALLY CONDUCTING POLYMER BLENDS</p> <p>(57) Abstract</p> <p>A method of forming a conductive polymer comprising a blend of at least one processable polymer, polyacetylene and a dopant by impregnating the processable polymer with a Ziegler-Natta catalyst; exposing the impregnated polymer to acetylene gas, whereby substantially linear molecules of polyacetylene are formed within a matrix of the processable polymer; and introducing a dopant into the polyacetylene, whereby a conductive blend is formed.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	LI	Liechtenstein
AU	Australia	LK	Sri Lanka
BE	Belgium	LU	Luxembourg
BR	Brazil	MC	Monaco
CF	Central African Republic	MG	Madagascar
CG	Congo	MR	Mauritania
CH	Switzerland	MW	Malawi
CM	Cameroon	NL	Netherlands
DE	Germany, Federal Republic of	NO	Norway
DK	Denmark	RO	Romania
FI	Finland	SE	Sweden
FR	France	SN	Senegal
GA	Gabon	SU	Soviet Union
GB	United Kingdom	TD	Chad
HU	Hungary	TG	Togo
JP	Japan	US	United States of America
KP	Democratic People's Republic of Korea		

- 1 -

ELECTRICALLY CONDUCTING POLYMER BLENDSTechnical Field

This invention relates to conductive polymers and, in particular, to blends containing polyacetylene treated with
5 electron donors or acceptors.

Background of the Invention

Conductive polymers are highly sought after at the present time to serve as substitutes for metals in a
10 variety of applications conducting electricity. For examples, conductive polymers hold promise in batteries, solar cells, semiconductors, electromagnetic shielding and even to replace traditional wiring.

Polyacetylene, or $(CH)_x$, is a material of considerable
15 interest since it can be rendered highly conductive by treatment with a variety of electron donors or acceptors. The light weight and potential low cost of this polymeric material suggest that it may be used in a variety of technological applications. In fact, working p-n junctions
20 and battery electrodes have been prepared by others. Unfortunately, $(CH)_x$ suffers three significant limitations with regard to practical applications. First, $(CH)_x$ is intractable (insoluble in all solvents and does not soften or melt) precluding fabrication of articles by conventional
25 techniques. Second, it is oxidatively unstable, thereby severely restricting its use in ambient conditions. Finally, the thermodynamically stable trans isomeric form of $(CH)_x$ renders the material brittle.

There exists a need for conducting polymers utilizing
30 the beneficial properties of polyacetylene but also having improved processability, stability and mechanical integrity.



- 2 -

Summary of the Invention

I have discovered that blends of polyacetylene and various other matrix materials, such as polyethylene and polystyrene can be formed and rendered conductive by appropriate doping techniques. My technique involves impregnating various polymers which are more processable than polyacetylene with a Ziegler-Natta catalyst, for example, $Ti(n-OBu)_4/Et_3Al$, and exposing the impregnated polymer to acetylene gas which results in polyacetylene formation throughout the polymer matrix. By proper selection of the matrix, oxidation of the polyacetylene can be reduced and the ratio of the components can be varied to control processability. Conductivity may be achieved by immersing the blend in an appropriate dopant, such as iodine, or by diffusion or implantation techniques.

My invention will be described below in connection with various examples; however, it should be obvious to those skilled in the art that changes and modifications can be made without departing from the spirit or scope of my claims. For example, other matrix materials, such as polybutadiene or other polymers, or mixtures of more than two polymers may be employed. Other Ziegler-Natta catalysts or their equivalents may be used to convert acetylene to the $(CH)_x$ polymer. Moreover, additional treatment steps can be employed to further stabilize my conductive blends and dopants other than iodine can be used.

Description of the Preferred Embodiment

The invention will be described in connection with the following non-limiting examples.



- 3 -

EXAMPLE I

A 0.3 mm thick, commercial low density polyethylene (LDPE) film was soaked in dry toluene for 24 hours to remove additives and immersed in a freshly-prepared solution containing dry toluene (60 ml), $\text{Ti}(\text{OBu})_4$ (3.75 ml) and Et_3Al (6 ml) in a Schlenk tube under argon. The tube was heated to ca. 70°C under a slow stream of argon for ca. 1.5 hr. to impregnate the film with the catalyst. After cooling to room temperature, the catalyst solution was removed with a syringe and the orange-brown LDPE film was washed with fresh toluene to remove surface catalyst residues. The Schlenk tube was then connected to a high vacuum line and the toluene was removed by pumping. Next, the film was allowed to contact acetylene gas (initial pressure ca. 700 torr) for various periods of time. Polymerizations were carried out at temperatures between -78 and 110°C . The high temperature polymerization was preferred since the polymerization rate is maximized without excessive melting of the matrix. During the high temperature polymerizations, the orange-brown catalyst impregnated LDPE film turned from blue to black as the acetylene diffuses into the film and polymerizes at the catalyst sites. Samples containing $> \text{ca. } 5 \text{ wt.}\%$ $(\text{CH})_x$ had a dull golden luster. The amount of $(\text{CH})_x$ in the blends was determined by acetylene uptake during polymerization and elemental analysis of the resulting materials, which typically contain ca. $0.15 \text{ wt.}\%$ and $0.20 \text{ wt.}\%$ of Ti and Al, respectively. The results from both methods were generally in good agreement.

Visible absorption spectra of thin films prepared at 110°C was consistent with the presence of the trans $(\text{CH})_x$ isomer. The films remained flexible and tough indefinitely. Samples containing $< \text{ca. } 5 \text{ wt.}\%$ $(\text{CH})_x$



- 4 -

soften between 120-150°C, although samples with ca. 6-10 wt.% (CH)_x did not soften up to 210°C. This was apparently due to the presence of a lightly crosslinked, three-dimensional (CH)_x network within the LDPE.

- 5 Exposure of the films to a 2% solution of I₂ in pentane for 24-48 hours resulted in ultimate conductivities (four probe method) of ca. 5Ω⁻¹cm⁻¹. A reasonably high conductivity was achieved at only 2 wt.% (CH)_x. That the conductivity is not due to solely surface-confined
- 10 (CH)_x was demonstrated by mounting the four platinum wires used for the conductivity measurements on the same side of the film and in another experiment mounting the pairs of wires on opposite sides. The results were essentially identical.

15

EXAMPLE II.

- A similar procedure was used, with some modification, to prepare polystyrene/(CH)_x blends. Since polystyrene was soluble in the catalyst solution described above, impregnated films were prepared by evaporation of the
- 20 solvent. After exposure to acetylene, black polystyrene/(CH)_x blends were obtained. Exposure to iodine vapor rendered the blends conductive in the range from about 10⁻¹⁰ to about 10¹Ω⁻¹cm⁻¹. The blends soften above 100°C depending on the blend composition.

In summary, a method for the preparation of novel conductive composites has been described. The resulting blends have reasonably high conductivities upon doping with iodine at a relatively low (CH)_x concentration.

The method of blend preparation described above should be applicable to a wide variety of systems provided that



- 5 -

the impregnated polymer does not react with the catalyst and that the monomer which is to form the second polymer is polymerizable by the catalyst. It should be pointed out that the invention is predominantly a novel means for preparing blends of two substantially linear polymers and should not be confused with well-known processes for preparing blends of crosslinked polymers (interpenetrating networks) by in-situ polymerization:

What I claim is:



- 1 Claim 1. A method of forming a conductive polymer
2 comprising a blend of at least one processable polymer,
3 polyacetylene and a dopant, the method comprising:
4 a) impregnating at least one processable
5 polymer with a Ziegler-Natta catalyst;
6 b) exposing said impregnated polymer to
7 acetylene gas, whereby substantially linear molecules
8 of polyacetylene are formed within a matrix of the
9 processable polymer; and
10 c) introducing a dopant into the polyacetylene,
11 whereby a conductive blend is formed.
- 1 Claim 2. The process of Claim 1 wherein the
2 processable polymer is polyethylene.
- 1 Claim 3. The process of Claim 1 wherein the
2 processable polymer is polystyrene.
- 1 Claim 4. The process of Claim 1 wherein the dopant
2 is iodine.
- 1 Claim 5. The process of Claim 1 wherein the
2 catalyst is $\text{Ti}(\text{n-OBu})_4/\text{Et}_3\text{Al}$.
- 1 Claim 6. The process of Claim 1 wherein the step
2 of impregnating the processable polymer with the catalyst
3 further comprises impregnating said polymer with said
4 catalyst at elevated temperatures.
- 1 Claim 7. The conductive polymer blend formed by
2 the method of Claim 1, 2 or 3.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US83/00079

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL ³ 08F/8/22, 255/02, 257/02		
U.S. CL. 252/500, 512, 518, 520, 524/80, 525/247, 275		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	252/500, 512, 518, 520 524/80 525/247, 275	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	U.S., A, 4,070,333, PUBLISHED 24 JANUARY 1978, JABLONER	1-7
A	U.S., A, 4,222,903, PUBLISHED 16 SEPTEMBER 1980, HEEGER ET AL	1-7
A	U.S., A, 4,304,890, PUBLISHED 08 DECEMBER 1981, SUZUKE ET AL	1-7
A	U.S., A, 4,329,440, PUBLISHED 11 MAY 1982, KOKUBO ET AL	1-7
<p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
04 MARCH 1983	18 MAR 1983 <i>Stanford M. Levin</i>	
International Searching Authority ³	Signature of Authorized Officer ²⁰	
ISA/US	STANFORD M. LEVIN	